Low Energy Singlets in the Excitation Spectrum of the Spin Tetrahedra System $Cu_2Te_2O_5Br_2$

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Abstract

Low energy Raman scattering of the s=1/2 spin tetrahedra system $Cu_2Te_2O_5Br_2$ is dominated by an excitation at 18 cm^{-1} corresponding to an energy $E_S = 0.6\Delta$, with Δ the spin gap of the compound. For elevated temperatures this mode shows a soft mode-like decrease in energy pointing to an instability of the system. The isostructural reference system $Cu_2Te_2O_5Cl_2$ with a presumably larger inter-tetrahedra coupling does not show such a low energy mode. Instead its excitation spectrum and thermodynamic properties are compatible with long range Néel-ordering. We discuss the observed effects in the context of quantum fluctuations and competing ground states.

Key words: Raman scattering, oxides, magnetic properties, phase transitions
PACS: 75.40.Gb, 75.40.Cx, 75.10.Jm, 78.30.-j

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1 Introduction

Raman light scattering is a powerful tool to investigate the low energy excitation spectrum of quantum spin systems realized, e.g. in transition metal oxides. This is based on its high sensitivity to all relevant degrees of freedom, especially to collective magnetic excitations as singlet modes or bound states, that are not observable in neutron scattering experiments. Singlet modes play an essential role in the description of many particle effects in the gapfull spin liquid phase of quantum spin systems [1]. Furthermore, scenarios have been developed for systems that are at a boundary to another competing phase, e.g. related to long range magnetic ordering [2]. Interesting in this respect are frustrated magnets like the Shastry-Sutherland lattice [3] or the Kagomé-lattice [4]. In this report we demonstrate, that a recently found quantum spin system based on weakly coupled Cu^{2+}-spin tetrahedra, $Cu_2Te_2O_5Br_2$ [5], shows low energy modes related to the spin system and an unusual instability that is easily tunable by the composition and the volume of the unit cell, i.e. a substitution of Br- by the smaller Cl-anions.

2 Results and Discussion

The crystal structure of $Cu_2Te_2O_5Br_2$ is shown in Fig. 1. It consists of Cu^{2+}-spin tetrahedra that are formed by an O- and Br-superexchange network of ions that is additionally supported by the *lone pair*-cation Te. Magnetic susceptibility measurements show a maximum at $T_{\chi_{max}} = 23$ K for this compound and at 30 K for the isostructural $Cu_2Te_2O_5Cl_2$. A strong reduction is evident at low temperatures, consistent with a spin gap system. A fit to these susceptibility data has been obtained with an intra-tetrahedra coupling of $J \approx 40$ K and a spin gap Δ of similar magnitude [5].

The excitation spectrum of such an individual tetrahedron is simple, however, the inherent degeneracy in the singlet sector may lead to interesting low temperature properties. The 16 states divide into a quintuplet, two triplets (with one state doubly degenerate) and two singlet states. The later singlets should form the ground state of the magnetic system. A seemingly negligible distortion of the tetrahedra should prefer one of them and shift the other to a small but higher energy. This low energy excited singlet state above the singlet ground state should only be observable in magnetic Raman scattering due to $\Delta S = 0$ Heisenberg exchange scattering.

In Fig. 2 Raman scattering spectra in (cc) polarization of the bromide and the chloride are compared at low temperatures. In $Cu_2Te_2O_5Br_2$ a pronounced mode is evident and attributed to a singlet state at $E_S = 18$ cm$^{-1} \approx 0.6\Delta$.

In addition, a pyramidal-shaped scattering continuum is observed centered at 61 cm^{-1} = 88 K with a total linewidth of 40 cm^{-1}. This continuum is attributed to a two-magnon-like scattering process [6] and its linewidth points to an appreciable inter-tetrahedra coupling. The polarization selection rule on the other hand supports a predominant exchange path along the crystallographic c-axis of the compound. This would justify models of 1D coupled tetrahedra [6]. The center energy corresponds very well to $2\Delta \approx 80$ K determined from the magnetic susceptibility [5]. In the chloride the low energy scattering is less pronounced and even more spread out. Also the phonon modes differ in frequency due to the different volume of the unit cell of the two compounds.

A study of the temperature dependence of the spectra in $Cu_2Te_2O_5Br_2$ shows a strong soft mode-like decrease of the frequency of the mode at $E_S = 18$ cm^{-1} pointing to some instability. Thermodynamic experiments indeed support this evidence since a broad bump at T_o=11.4 K is observed in the specific heat together with a kink in the magnetic susceptibility [7]. The transition temperature shows a well pronounced increase with a magnetic field. In contrast, for $Cu_2Te_2O_5Cl_2$ the specific heat shows a lambda-like anomaly at T_N=18.2 K and essentially no effect of a magnetic field. Here, all observations are consistent with long-range Néel-Ordering.

3 Conclusion

The peculiar experimental observations in these two Cu-Oxo-Halides give evidence that, although structurally related, their low energy excitation spectrum and ground state properties are very distinct. Although details of the electronic band structure, hopping elements and especially the important inter-tetrahedra exchange coupling constants of these systems are unknown, some conclusions can be made. In first approximation and neglecting the electronic difference between Cl- and Br-anions the main difference is the 7% larger unit cell volume of $Cu_2Te_2O_5Br_2$, that should be related to a smaller inter-tetrahedra coupling. This coupling is evidenced in a more concentrated spectral weight of the two-magnon-like continuum in Raman scattering and the smaller transition temperature. In the proposed scenario the transition itself lifts the degeneracy of the singlet states. This however does not necessarily mean that a large structural distortion is involved. A careful investigation of the optical phonon excitations does not give any evidence for superlattice peaks. In this sense the phenomenology is much different from a spin-Peierls transition, as observed in $CuGeO_3$, or the charge ordering related instability in NaV_2O_5, although in these compounds low energy singlets are observed as well [8,9]. Further studies are underway to understand this material.

Acknowledgement: We are grateful for helpful discussions with H. Kageyama, Yu. Ueda, and K. Ueda. This work was supported in part by the DFG through SPP1073 and the Swiss Science Foundation under grant nr. 21-63749.

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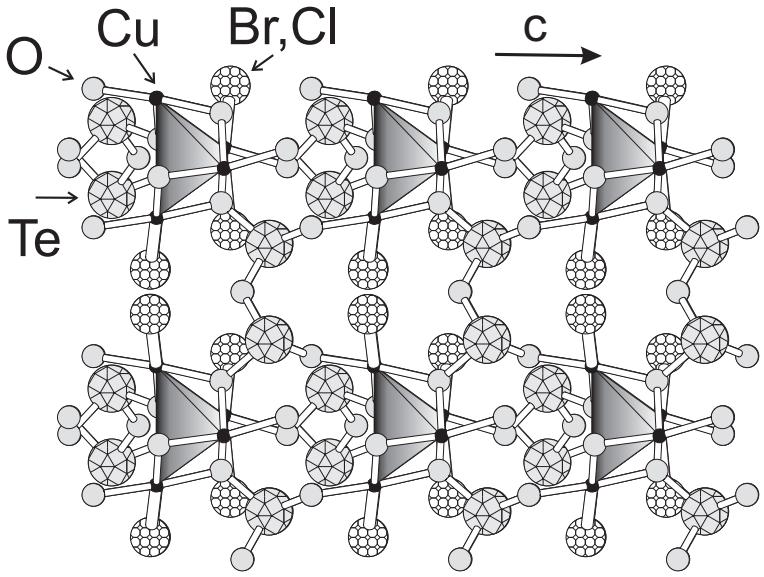

Fig. 1. Crystal structure of $Cu_2Te_2O_5X_2$, X=Br or Cl, with hatched Cu-tetrahedra.

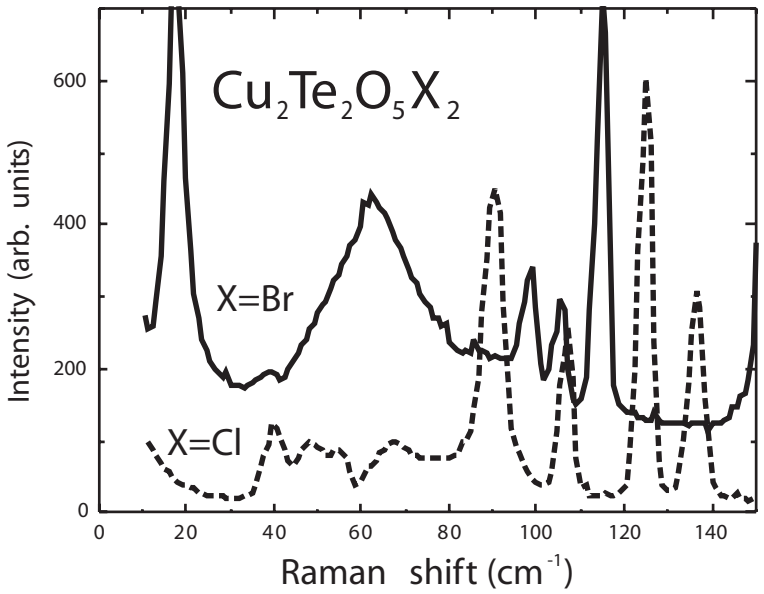

Fig. 2. Raman spectra of $Cu_2Te_2O_5Br_2$ and the isostructural $Cu_2Te_2O_5Cl_2$ at low temperatures (T=3K) in c-axis polarization (cc). The spectrum of $Cu_2Te_2O_5Br_2$ has been shifted upwards by 100 counts.